Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

The electrooxidation-induced structural changes of gold di-superatomic molecules: Au_{23} vs. Au_{25}

Shota Matsuo,[a] Seiji Yamazoe,[ab] Jing-Qiang Goh,[cd] Jaakko Akola,[cd] Tatsuya Tsukuda*[ab]

[a] *Department of Chemistry, School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan*

[b] *Elements Strategy Initiative for Catalysts and Batteries (ESICB), Kyoto University, Katsura, Kyoto 615-8520, Japan*

[c] *Department of Physics, Tampere University of Technology, P.O. Box 692, FI-33101 Tampere, Finland.*

[d] *COMP Centre of Excellence, Department of Applied Physics, Aalto University, FI-00076 Aalto, Finland.*

---

1. Experimental

A. Chemicals

Milli-Q grade water was employed exclusively in the present study. All reagents and solvents were commercially available and were used as received without further purification.

B. Synthesis

$Au_{38}(SC_2H_4Ph)_{24}$

$Au_{38}(SC_2H_4Ph)_{24}$ was synthesized using a previously reported method.[1] Briefly, a mixture of $HAuCl_4 \cdot 4H_2O$ (2.0 mmol) and reduced form glutathione (1.0 mmol) in acetone (80 mL) was stirred for 20 min at room temperature. The mixture was subsequently stirred for an additional 20 min in an ice bath, after which a solution of $NaBH_4$ (20 mmol, dissolved in 20 mL of water) was rapidly added with vigorous stirring. After 20 min, the supernatant was removed by decanting, and the remaining black solid was dried under vacuum. One fourth of the resulting solid product was added to a mixture of water (6 mL), ethanol (0.3 mL), toluene (2 mL), and 2-phenylthanethiol (2 mL) and the biphasic solution was stirred at 80 °C. After approximately 15 h, the organic layer was thoroughly washed with water and evaporated. Then the residual sample was washed with a mixture of water and methanol (1:4), followed by pure methanol. Finally, the crude $Au_{38}(SC_2H_4Ph)_{24}$ was extracted with toluene and pure $Au_{38}(SC_2H_4Ph)_{24}$ was obtained by high pressure liquid chromatography (HPLC, Japan Analytical Industry Co., Ltd., LC-908) with gel permeation chromatography (GPC) column (Japan Analytical Industry Co., Ltd., JAIGEL-W253). Toluene was used as the mobile phase at a flow rate of 3.5 mL/min.

$[Au_{25}(PPh_3)_{10}(SC_2H_4Ph)_5Cl_2]Cl_2$

$[Au_{25}(PPh_3)_{10}(SC_2H_4Ph)_5Cl_2]Cl_2$ was prepared using a previously reported method with some modifications.[2–5] $NaBH_4$ (0.50 mmol) was slowly added to a solution of $AuCl(PPh_3)$ (0.51 mmol) in absolute ethanol (12 mL) over 7 min. After stirring at room temperature for 2 h, the mixture was poured into hexane (200 mL). Filtration using a membrane filter (pore diameter: 0.2 μm) was used to collect the brown solid product, which was then washed with hexane, CH_2Cl_2/hexane (1:1, 15 mL), and CH_2Cl_2/hexane (3:1, 2.5 mL). The resulting solid was dissolved in CH_2Cl_2 and the solution was filtered. After evaporation of the solvent, phosphine-stabilized Au clusters were obtained as a dark brown solid. A 20 mg quantity of the obtained solid was subsequently reacted with 2-phenylethanethiol (37μL) in chloroform (30 mL) with stirring at 55 °C. After 1 h, the organic layer was evaporated and washed with hexane, toluene, ethyl acetate, and diethyl ether. Finally, pure $[Au_{25}(PPh_3)_{10}(SC_2H_4Ph)_5Cl_2]Cl_2$ was extracted with ethanol.

C. Characterization

UV-Visible-NIR optical spectrometry

UV-vis-NIR absorption spectra were recorded on V-670 (JASCO, Japan) and Agilent 8453 (Agilent, Japan) spectrophotometer.

Matrix-assisted laser desorption ionization (MALDI) mass spectrometry

MALDI-time-of-flight (TOF) mass spectra were acquired using a mass spectrometer (Shimadzu Axima-CFR) coupled with a N_2 laser (337 nm). Samples for mass analysis were prepared using trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]-malononitrile (DCTB) as a matrix.

2. Results

A. Characterization of $Au_{38}(SC_2H_4Ph)_{24}$

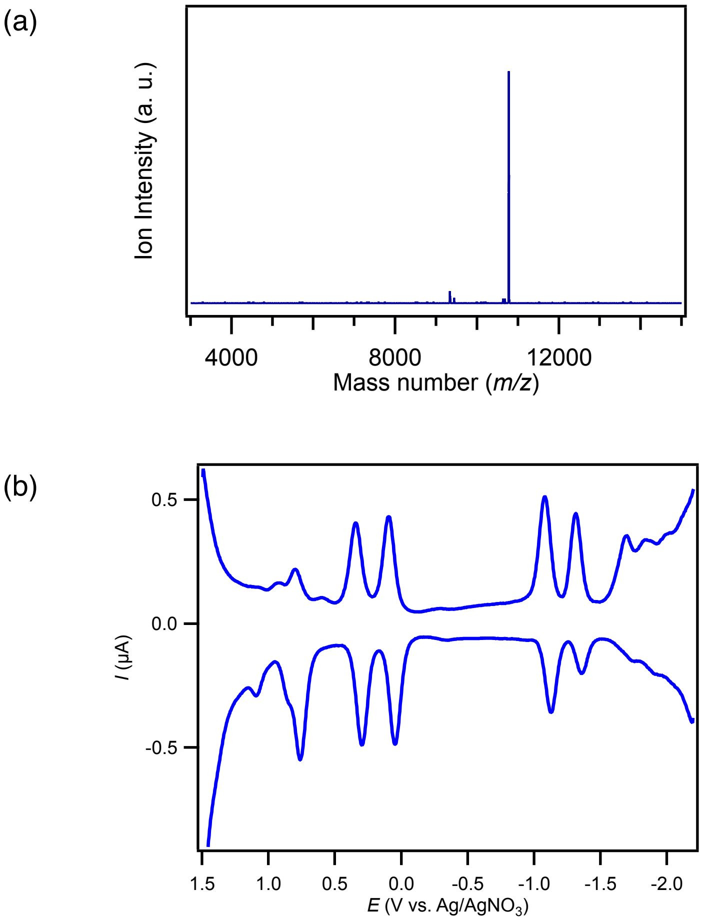


Figure S1. (a) MALDI-TOF mass spectrum and (b) differential pulse voltammogram (peak amplitude of 0.05 V, pulse width of 0.05 s, increment potential of 4 mV, and pulse period of 0.1 s).

B. Characterization of $[Au_{25}(PPh_3)_{10}(SC_2H_4Ph)_5Cl_2]Cl_2$

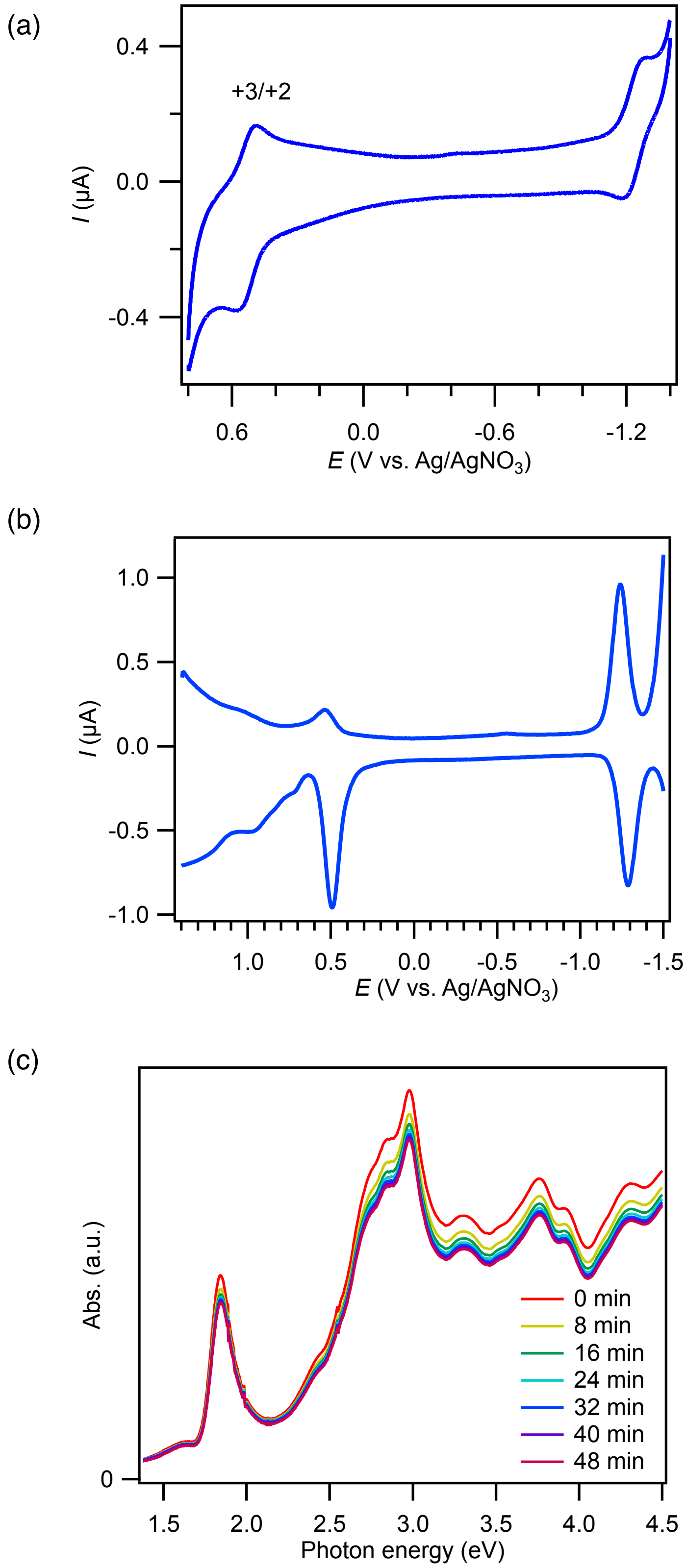


Figure S2. (a) Cyclic voltammogram (scan rate: 0.2 V/s), (b) differential pulse voltammogram (peak amplitude of 0.05 V, pulse width of 0.05 s, increment potential of 4 mV, and pulse period of 0.1 s) and (c) optical absorption spectra during electrolysis at 0.35 V.

C. Theoretical calculations of $[Au_{38}(SC_2H_4Ph)_{24}]^{0+/2+}$

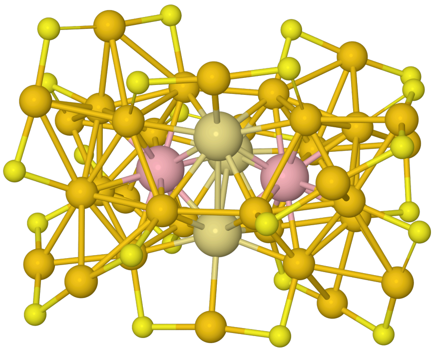
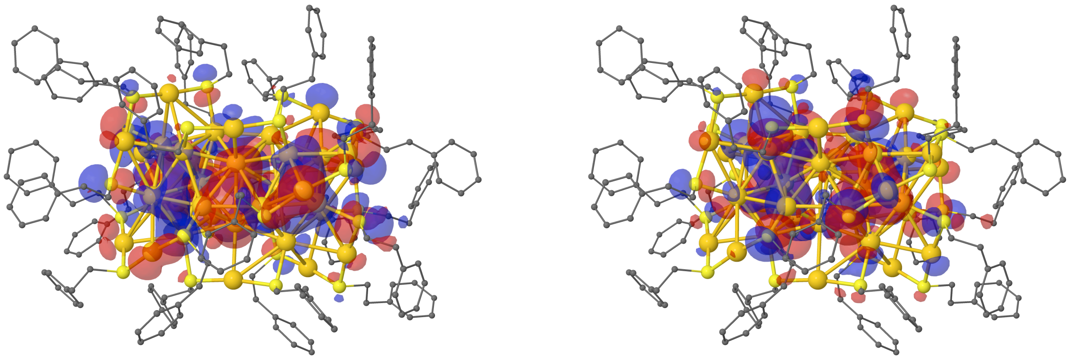


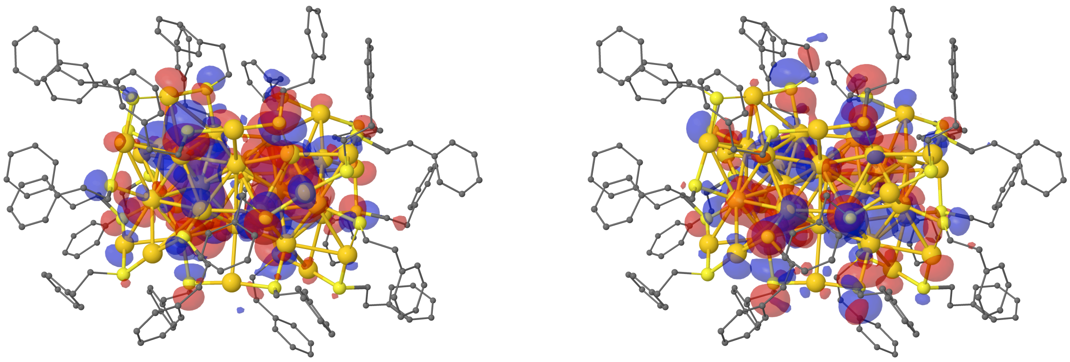
Figure S3. Illustration of the optimized core structure of $\mathbf{1}^{q+}$ (q=0 or 2). The three Au atoms (Au_F) of face-sharing mode between the two Au_{13} units are highlighted in khaki color. The centers (Au_I) of individual Au_{13} units are highlighted in light-pink color. Color code of the other atoms: Au, gold and S, yellow. The carbon and hydrogen atoms are omitted for clarity.

Table S1. The computed bond distances of the chosen group of atoms in the core structure of $\mathbf{1}^{q+}$ (q=0 or 2). The three Au atoms of face-sharing mode and the centers of individual Au_{13} units are labeled as Au_F and Au_I, respectively. Geometric optimizations of **1** in these two different charge states indicate that the structural change of Au_{23}^{9+} is negligible.

Selected Bond Distances	$\mathbf{1}^{0+}$	$\mathbf{1}^{2+}$
Au_I-Au_I	4.17Å	4.14Å
Au_I-neighboring Au atoms	2.870±0.028 Å	2.882±0.028 Å
Au_F-Au_F	3.443±0.026 Å	3.443±0.034 Å



(a) LUMO of $\mathbf{1}^{0+}$ (b) HOMO of $\mathbf{1}^{0+}$ (degenerate)



(c) LUMO of $\mathbf{1}^{2+}$ (d) HOMO of $\mathbf{1}^{2+}$

Figure S4. (a) LUMO of $\mathbf{1}^{\mathbf{0+}}$, (b) HOMO of $\mathbf{1}^{\mathbf{0+}}$, (c) LUMO of $\mathbf{1}^{2+}$, and (d) HOMO of $\mathbf{1}^{2+}$ obtained by the program GPAW and PBE functional. Notice that the LUMO and HOMO of $\mathbf{1}^{2+}$ share the same symmetry of $1\pi^*$. One of the degenerate HOMO($1\pi^*$) orbitals in $\mathbf{1}^{0}$ has been promoted to become the LUMO of $\mathbf{1}^{2+}$. Color code: Au, gold; S, yellow; C, dim gray. The hydrogen atoms are omitted for clarity and the visualization of molecular orbital states are displayed using a cutoff value of 0.03 a.u.

D. Theoretical calculations of $[Au_{25}(PPh_3)_{10}(SC_2H_4Ph)_5Cl_2]^{2+/3+}$

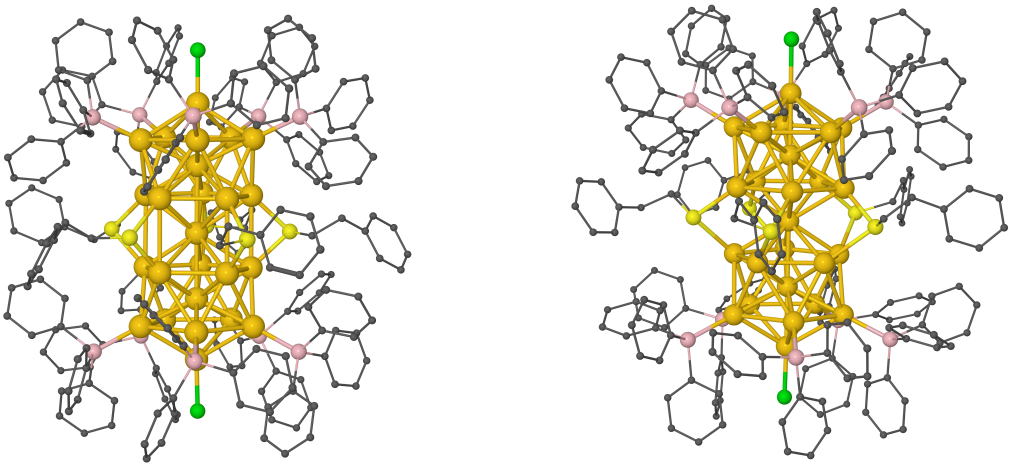
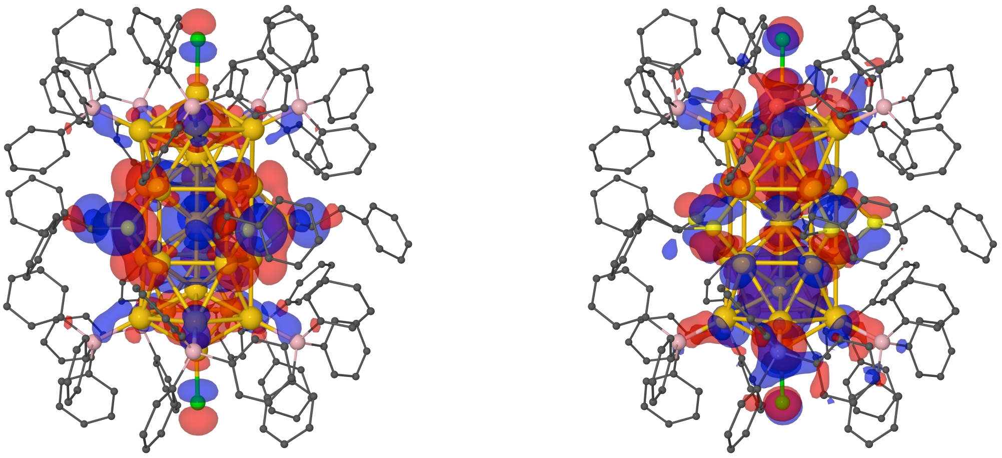
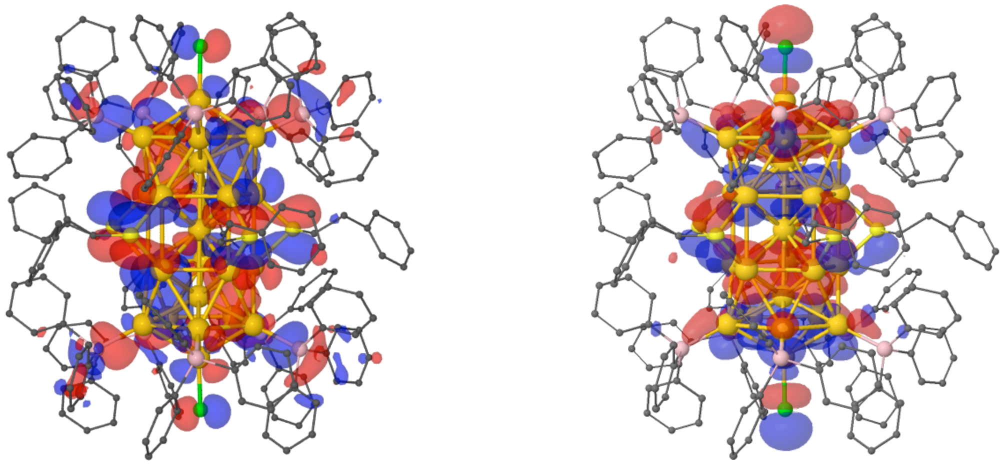

(a) (b)

Figure S5. Initial structures for $\mathbf{2}^{3+}$ with (a) eclipsed and (b) staggered configuration, respectively. Geometry optimizations based on these initial structures result in the ordinary core framework of $\mathbf{2}^{2+}$. Color code: Au, gold; P, pink; S, yellow; Cl, light green; C, dim gray. The hydrogen atoms are omitted for clarity.



(a) HOMO, -7.075 eV (b) HOMO-1, -7.321 eV



(c) HOMO-2, -7.329 eV (d) HOMO-3, -7.379 eV

Figure S6. (a) HOMO, (b) HOMO-1, (c) HOMO-2, and (d) HOMO-3 of **2**$^{2+}$ obtained by the program GPAW and PBE functional. The eigenvalues demonstrate that these states are close to each other and their energetic ordering can be sensitive to external factors such as neighboring localized orbital states. Color code: Au, gold; P, pink; S, yellow; Cl, light green; C, dim gray. The hydrogen atoms are omitted for clarity and the visualization of molecular orbital states are displayed using a cutoff value of 0.03 a.u.

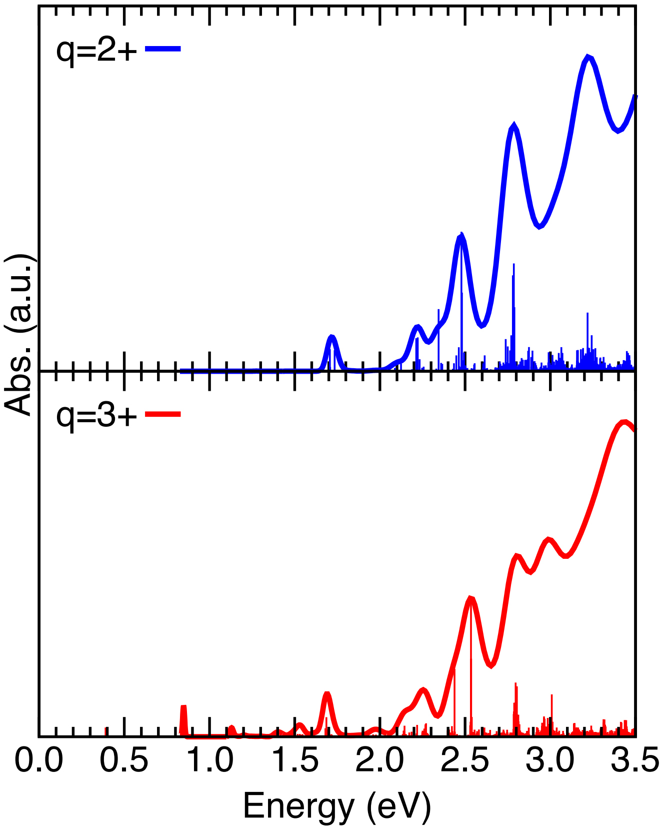


Figure S7. Simulated optical absorption spectra of $\mathbf{2}^{2+}$ and $\mathbf{2}^{3+}$ in full scale. The individual transition values have been multiplied by a factor of 20. Spin-polarization effects of $\mathbf{2}^{3+}$ (odd number of electrons) are included in the calculation.

E. TEM observation of electrooxidation sample of $[Au_{25}(PPh_3)_{10}(SC_2H_4Ph)_5Cl_2]^{2+}$

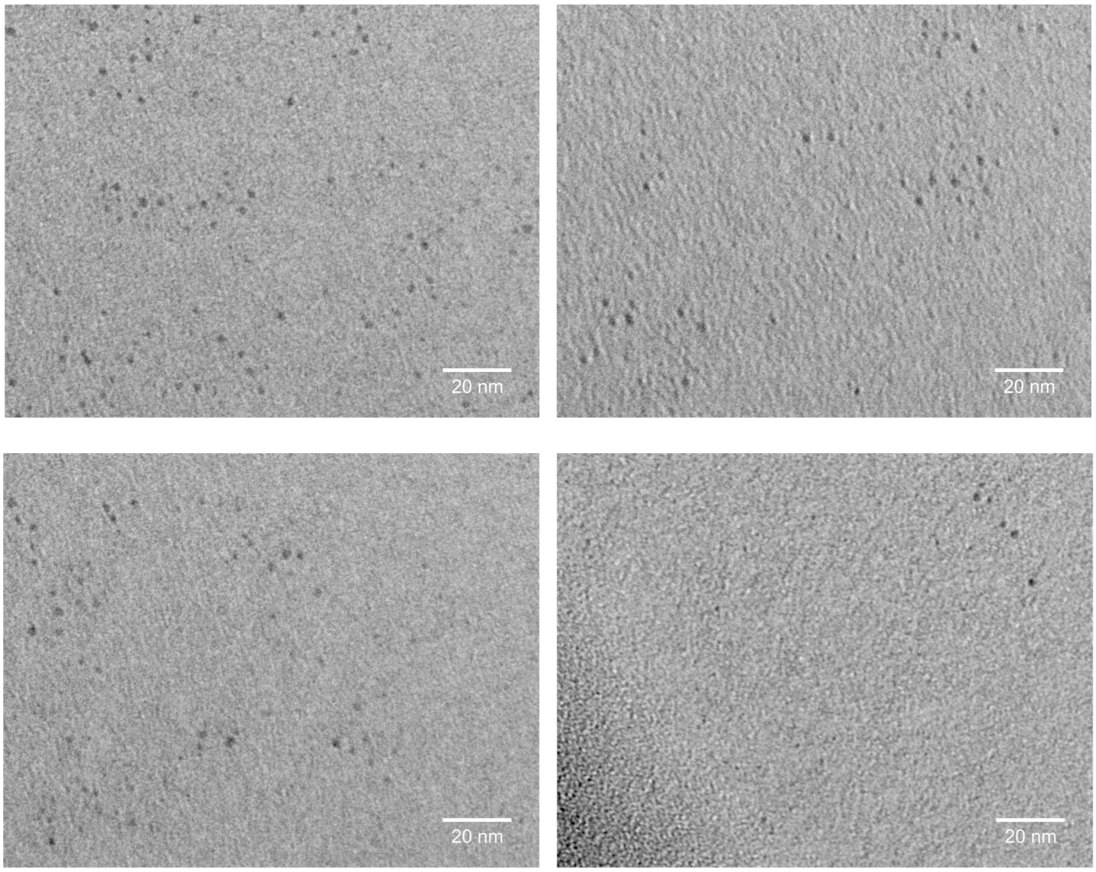


Figure S8. TEM images of one-electron oxidation sample of $\mathbf{2}^{2+}$. The sample included ~30% of unoxidized $\mathbf{2}^{2+}$ because the initial sample included ~0.15 mg of $\mathbf{2}^{2+}$ and the amount of generated oxidation product was estimated to be 0.10 mg from the transferred charge amount of 1.15 mC.

References

(1) H. Qian, Y. Zhu and R. Jin, *ACS Nano*, 2009, **3**, 3795.
(2) G. H. Woehrle, M. G. Wamer and J. E. Hutchison, *J. Phys. Chem. B,* 2002, **106**, 9979.
(3) Y. Shichibu, Y. Negishi, T. Tsukuda and T. Teranishi, *J. Am. Chem. Soc.*, 2005, **127**, 13464.
(4) Y. Shichibu, Y. Negishi, T. Watanabe, N. K. Chaki, H. Kawaguchi and T. Tsukuda, *J. Phys. Chem. C*, 2007, **111**, 7845.
(5) S. Park and D. Lee, *Langmuir*, 2012, **28**, 7049.